A SYNOPSIS OF THE CHEMICAL/PHYSICAL PROPERTIES OF SEAWATER

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ABSTRACT

Engineering materials exposed to seawater are subjected to various deteriorating reactions throughout their lifetime. Chemical reactions that take place in seawater can be attributed to the solvent properties of water, ion-water and ion-ion interactions. Many properties of seawater, such as density, thermal expansion, temperature of maximum density, viscosity, speed of sound, vapor pressure, etc., change with changing salt content. A knowledge of the way these parameters change, as well as processes that cause the changes, is essential to the design of systems that will effectively operate in the ocean. The following is a synopsis of the chemical and physical properties of seawater that are known to have an impact on ocean engineering.

CHEMICAL NATURE OF SEAWATER

Since the oceans consist of 96.5% water, many characteristics of ocean water are similar to those of fresh water. In marine chemistry the solvent properties of water are of primary interest. The solubility of substances, especially ionic compounds, is much higher in water than in other solvents. This high solubility results from the atomic structure

TABLE I

The Major Ions of Seawater.

Ion	Symbol	g kg^{-1} at S = 35	% as free ion	% by weight of the total major constituents
Sodium	Na +	10.78	99	30.66
Magnesium	Mg^{2+}	1.283	87	3.65
Calcium	Ca^{2+}	0.4119	91	1.17
Potassium	K +	0.399	99	1.13
Strontium	Sr^{2+}	0.0079	90	0.02
Chloride	Cl$^-$	19.344	100	55.03
Sulfate	SO$_4{}^{2-}$	2.711	50	7.71
Bicarbonate	HCO$_3{}^-$	0.1135	67	0.32
Bromide	Br$^-$	0.0672	100	0.19
Borate	B(OH)$_3$	0.0203		0.06
Carbonate	CO$_3{}^{2-}$	0.0116		0.03
Borate	B(OH)$_4{}^-$	0.0066	10	0.02
Fluoride	F$^-$	0.0012	100	0.01
				100.00

of the water molecule with the hydrogen atoms tightly bound to oxygen and separated by a 105° angle, giving the water molecule a dipolar charge balance. Because of their dipolar configuration, water molecules tend to interact strongly with each other, as well as with other solute molecules. This property makes water a near-universal solvent and makes the ocean a chemical soup containing almost all elements in solution in some amount.

A. Major Ions

The major ions in seawater can be defined as those that make a significant contribution to measured salinity. This definition is generally taken to mean elements present in concentrations greater than 1 part per million (ppm) in oceanic water. The chemical and physicochemical properties of seawater can be attributed to the 13 major ions that make up over 99.9% of the material dissolved in seawater. These ions are listed in Table I.

These major ions exist primarily as free ions, but small amounts form ion pairs due to the electrostatic interaction between the highly charged ions in solution. Ion pairing becomes significant for sulfate ions, which can form ion pairs with magnesium, calcium,

and strontium. Only half of the sulfate in seawater exists as a free ion. In a later section the importance of these sulfate ion pairs in attenuating sound in seawater will be discussed.

The primary source of major ions to the ocean is riverine input. Once these ions enter the ocean, their residence time is very long compared to the mixing time for the oceans. The total salt content (or salinity) of a seawater sample may change with depth or location in the ocean, due to precipitation, evaporation or mixing. However, the ratio of the major ions varies only slightly in the open ocean. This concept, known as constancy of composition, or Marcet's principle, results from the fact that the oceans are well mixed in relation to the major constituents.

B. Trace Elements

Those elements found in seawater at levels below 1 ppm are considered trace elements. While the dissolved gases and some nutrient elements are undeniably trace species, they are discussed elsewhere in this paper. Table II lists the remaining trace elements in seawater, along with their residence times. These elements exhibit an enormous range of chemical reactions and enter widely into the biochemical and geochemical cycles of the ocean. While the concentrations and residence times reported in Table II are accepted averages for trace elements, the values have limited meaning because of large variations both geographically and with depth, and the limited, reliable oceanic profiles for many of these elements.

Like the major ions, riverine input is the primary source of trace elements to the ocean, accounting for over 90% of the total. Other significant inputs come from ice transport (mainly from Antarctica) and atmospheric dust. Removal of trace elements from the ocean results from a combination of adsorption onto particulate material, biological uptake, and perhaps precipitation for a few elements (e.g., Sr, Ba). Such processes result in short residence times for trace elements and make their concentrations low in seawater.

TABLE II

Mean Concentration of Trace Elements in Seawater Exclusive
of Nutrients and Dissolved Gases, from Broecker and Peng (1982).

Element	Symbol	Concentration (μmol kg^{-1})	Residence time (years)
Lithium	Li	2.5×10^1	5.7×10^5
Rubidium	Rb	1.4	3.0×10^6
Iodine	I	4.4×10^{-1}	3.4×10^5
Barium	Ba	1.0×10^1	8.8×10^3
Indium	In	$(1.0 \times 10^{-6})^*$	—
Zinc	Zn	6.0×10^{-3}	5.1×10^2
Iron	Fe	(1.0×10^{-3})	5.4×10^1
Aluminum	Al	(3.0×10^{-2})	6.2×10^2
Molybdenum	Mo	1.1×10^{-1}	8.2×10^5
Selenium	Se	1.7×10^{-3}	2.6×10^4
Tin	Sn	(4.0×10^{-6})	—
Copper	Cu	4.0×10^{-3}	9.7×10^2
Arsenic	As	2.3×10^{-2}	3.9×10^4
Uranium	U	1.3×10^{-2}	$\sim 5 \times 10^5$
Nickel	Ni	8.0×10^{-3}	8.2×10^3
Vanadium	V	2.3×10^{-2}	4.5×10^4
Manganese	Mn	5.0×10^{-3}	1.3×10^3
Titanium	Ti	$(<2.0 \times 10^{-2})$	3.7×10^3
Antimony	Sb	1.2×10^{-3}	5.7×10^3
Cobalt	Co	(3.0×10^{-5})	3.4×10^2
Cesium	Cs	2.2×10^{-3}	3.3×10^5
Cerium	Ce	2.0×10^{-5}	1.4×10^3
Yttrium	Y	1.5×10^{-4}	7.4×10^2
Silver	Ag	(2.5×10^{-5})	3.5×10^2
Lanthanum	La	3.0×10^{-5}	3.2×10^2
Cadmium	Cd	7.0×10^{-4}	—
Tungsten	W	6.0×10^{-4}	—
Germanium	Ge	7.0×10^{-5}	—
Chromium	Cr	4.0×10^{-3}	8.2×10^3
Thorium	Th	$(<3 \times 10^{-6})$	—
Scandium	Sc	(1.5×10^{-5})	—
Lead	Pb	1.0×10^{-5}	8.1×10^1
Mercury	Hg	(5.0×10^{-6})	5.6×10^2
Gallium	Ga	(3.0×10^{-4})	9.0×10^3
Bismuth	Bi	(1.0×10^{-4})	—
Niobium	Nb	$(<5 \times 10^{-5})$	—
Thallium	Tl	6.0×10^{-5}	—
Gold	Au	(2.5×10^{-5})	9.7×10^4
Praseodymium	Pr	4.0×10^{-6}	3.1×10^3

*The values in parentheses are speculative.

C. Dissolved Gases

Every atmospheric gas is found dissolved in seawater. Unlike the major seawater components, however, the primary source for dissolved gases in seawater is not rivers but the atmosphere. Dissolution of atmospheric gases in seawater can be described by Henry's Law, which describes the relationship between the partial pressure of a gas in solution, P_G, and its concentration, C_G, such that

$$P_G = K_G C_G . \tag{1}$$

TABLE III

Constants for Calculation of Bunsen Solubility Coefficients, β, According to Equation (3).

Gas	A_1	A_2	A_3	B_1	B_2	B_3	Ref.
N_2	− 59.6274	85.7661	24.3696	− 0.051580	0.026329	− 0.0037252	1
O_2	− 58.3877	85.8079	23.8439	− 0.034892	0.015568	− 0.0019387	1
Ar	− 55.6578	82.0262	22.5929	− 0.036267	0.016241	− 0.0020114	1
Ne	− 39.1971	51.8013	15.7699	− 0.124695	0.078374	− 0.0127972	2
He	− 34.6261	43.0285	14.1391	− 0.042340	0.022624	− 0.0033120	2
CH_4	− 68.8862	101.4956	28.7314	− 0.076146	0.043970	− 0.0068672	3
CO	− 47.6148	69.5068	18.7397	0.045657	− 0.040721	0.0079700	3
H_2	− 47.8948	65.0368	20.1709	− 0.082225	0.049564	− 0.0078689	3
N_2O	− 59.5965	97.3066	24.1406	− 0.058420	0.033193	− 0.0051313	4

[1]Weiss (1970), [2]Weiss (1971), [3]Wiesenburg and Guinasso (1979), [4]Weiss and Price (1980).

K_G is the Henry's Law constant, which is a function of the molecular properties of the gas, temperature, salinity, and total pressure. When expressing the gas concentration in terms of the volume of gas per volume of solution, Henry's Law relates the concentration of an ideal gas in solution (C^*) to a constant times the partial pressure of the gas above the solution

$$C^* = \beta P_G \, , \qquad (2)$$

where β is the Bunsen coefficient and P_G is the partial pressure of the gas. The Bunsen solubility of a gas as a function of temperature and salinity can be described by a combined equation that expresses the temperature dependence of solubility at constant salinity by an integrated form of Van't Hoff's equation and uses the Setchenow relation to describe the salinity effect. The combined equation (Weiss, 1970) is

$$ln \, \beta = A_1 + A_2 \, (100/T) + A_3 \, ln \, (T/100) + S \, [B_1 + B_2 \, (T/100)$$
$$+ B_3 \, (T/100)^2] \, , \qquad (3)$$

where A_i and B_i are constants, T is the temperature in Kelvins, and S is the salinity. The constants necessary to calculate Bunsen coefficients for nitrogen, oxygen, argon, neon, helium, methane, carbon monoxide, hydrogen, and nitrous oxide are given in Table III.

For nitrogen, oxygen, argon, and the inert noble gases, the atmospheric concentrations are relatively constant; thus, the atmospheric equilibrium solubility (AES) of these gases

TABLE IV

Constants for Calculation of Atmospheric Equilibrium Solubilities of Various Gases,
According to Equation (4). Coefficients are given for both μmol kg^{-1} and cm^3 dm^{-3} calculations.

Gas	A_1	A_2	A_3	A_4	B_1	B_2	B_3
	Constants to yield C* in μmol kg^{-1}						
N_2	-172.4965	248.4262	143.0738	-21.7120	-0.049781	0.025018	-0.0034861
O_2	-173.4292	249.6339	143.3483	-21.8492	-0.033096	0.014259	-0.0017000
Ar	-173.5146	245.4510	141.8222	-21.8020	-0.034474	0.014934	0.0017729
Ne	-160.2630	211.0969	132.1657	-21.3165	-0.122883	0.077055	-0.0125568
He	-152.9405	196.8840	126.8015	-20.6767	-0.040543	0.021315	0.0030732
	Constants to yield C* in cm^3 dm^{-3}						
N_2	-173.2221	254.6078	146.3611	-22.0933	-0.054052	0.027266	-0.0038430
O_2	-173.9894	255.5907	146.4813	-22.2040	-0.037362	0.016504	-0.0020654
Ar	-174.3732	251.8139	145.2337	-22.2046	-0.038729	0.017171	-0.0021281
Ne	-166.8040	225.1946	140.8863	-22.6290	-0.127113	0.079277	-0.0129095
He	-163.4207	216.3442	139.2032	-22.6202	-0.044781	0.023541	-0.0034266

can be easily calculated from Eq. (2), if the temperature, salinity, relative humidity, and
vapor pressure are known. To simplify the calculation Weiss (1970) developed an equation
for calculating AES from moist air as a function of only temperature and salinity:

$$ln\ C^* = A_1 + A_2\ (100/T) + A_3\ ln\ (T/100) + A_4\ (T/100)$$
$$+ S\ [B_1 + B_2\ (T/100) + B_3\ (T/100)^2]\ , \qquad (4)$$

where C^* is the AES solubility in micromoles per kilogram (or other appropriate units).
The coefficients necessary to calculate the AES for nitrogen, oxygen, argon, neon, and
helium in micromoles per kilogram (μmol kg^{-1}) and cubic centimeters per cubic deci-
meter (cm^{3}dm^{-3}) are given in Table IV. Since oxygen and nitrogen are the most abundant
gases found in seawater, tables of their atmospheric equilibrium solubilities in seawater,
as a function of temperature and salinity, are given in Tables V and VI, respectively.

The vertical distribution of dissolved oxygen in the oceans is shown in Figure 1. Near
the sea surface, the oxygen content is high due to atmospheric equilibrium, injection of
air bubbles and photosynthetic production. The oxygen concentration decreases with depth
as increased net animal respiration and microbial organic decomposition remove oxygen.
The oxygen levels increase below the minimum due to horizontal advection of oxygen-
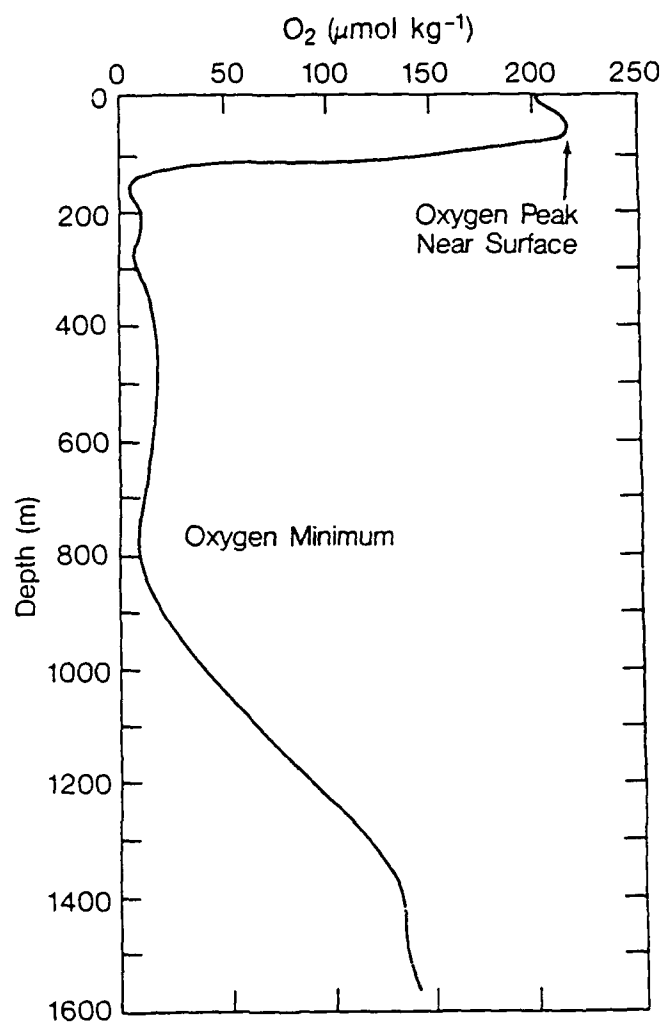rich bottom water that, having been at the surface more recently than water at intermediate

FIG. 1. Vertical distribution of dissolved oxygen in the oceans, from Sverdrup, Johnson, and Fleming (1942).

depth, still contains appreciable dissolved oxygen. Deep water oxygen levels can be used to trace water masses throughout the ocean.

D. Nutrients

Many inorganic chemical constituents of seawater are intimately involved in the oceanic life processes. These compounds include water, oxygen, nitrogen, phosphorus, silicon, carbon (carbonate), and to a lesser extent such trace elements as iron, manganese, molybdenum, zinc, cobalt, copper, and vanadium. Except for water, oxygen, and carbon,

TABLE V

Solubility of Oxygen in Seawater in μmol kg^{-1} from Kester (1975).

| t (°C) | Salinity |
	0	4	8	12	16	20	24	28	31	33	35	37	39
−1	469.7	455.5	441.7	428.3	415.4	402.8	390.6	378.8	370.2	364.6	359.0	353.5	348.2
0	456.4	442.7	429.4	416.5	404.0	391.9	380.1	368.7	360.4	354.9	349.5	344.2	339.0
1	443.8	430.6	417.7	405.3	393.2	381.5	370.1	359.0	351.0	345.7	340.5	335.4	330.3
2	431.7	418.9	406.5	394.5	382.8	371.5	360.5	349.8	342.0	336.9	331.8	326.9	322.0
3	420.2	407.9	395.9	384.2	372.9	361.9	351.3	340.9	333.4	328.5	323.6	318.8	314.1
4	409.3	397.3	385.7	374.4	363.5	352.9	342.6	332.5	325.2	320.4	315.7	311.1	306.5
5	398.8	387.2	375.9	365.0	354.4	344.1	334.1	324.4	317.4	312.7	308.1	303.6	299.2
6	388.7	377.5	366.6	356.0	345.8	335.8	326.1	316.7	309.8	305.3	300.9	296.5	292.2
7	379.1	368.2	357.7	347.4	337.5	327.8	318.4	309.3	302.6	298.3	294.0	289.7	285.5
8	369.9	359.4	349.1	339.2	329.6	320.2	311.1	302.2	295.8	291.5	287.3	283.2	279.2
9	361.1	350.9	341.0	331.3	322.0	312.9	304.0	295.4	289.2	285.0	281.0	277.0	273.0
10	352.6	342.7	333.1	323.7	314.6	305.8	297.2	288.9	282.8	278.8	274.8	271.0	267.1
11	344.5	334.9	325.5	316.5	307.6	299.1	290.7	282.6	276.7	272.8	269.0	265.2	261.5
12	336.7	327.3	318.3	309.5	300.9	292.6	284.5	276.6	270.8	267.0	263.3	259.6	256.0
13	329.2	320.1	311.3	302.8	294.4	286.3	278.5	270.8	265.2	261.5	257.9	254.3	250.8
14	322.0	313.2	304.7	296.3	288.2	280.4	272.7	265.3	259.8	256.2	252.7	249.2	245.8
15	315.1	306.5	298.2	290.1	282.3	274.6	267.1	259.9	254.6	151.1	247.7	244.3	240.9
16	308.5	300.1	292.0	284.2	276.5	269.1	261.8	254.7	249.6	246.2	242.8	239.5	236.3
18	295.9	288.0	280.3	272.9	265.6	258.5	251.7	245.0	240.1	236.9	233.7	230.6	227.5
20	284.2	276.7	269.5	22.4	255.5	248.8	242.3	235.9	231.2	228.2	225.2	222.2	219.3
22	273.4	266.3	259.4	252.7	246.1	239.7	233.5	227.5	223.0	220.1	217.3	214.4	211.6
24	263.3	256.5	250.0	243.6	237.3	231.3	225.4	219.6	215.4	212.6	209.9	207.2	204.5
26	253.8	247.4	241.2	235.1	229.2	223.4	217.7	212.2	208.2	205.6	202.9	200.4	197.8
28	245.0	238.9	232.9	227.1	221.5	215.9	210.6	205.3	201.5	198.9	196.4	194.0	191.5
30	236.7	230.9	225.2	219.7	214.2	209.0	203.8	198.8	195.1	192.7	190.3	188.0	185.7
32	228.9	223.4	217.9	212.6	207.5	202.4	197.5	192.7	189.2	186.9	184.6	182.3	180.1

these elements are classified as micronutrient elements. They are defined as materials essential to the growth of plants and animals that are present in such small concentrations that they may b ˙ome depleted in the water column, thereby limiting additional growth.

Nitrogen, phosphorus, silicon, and inorganic carbon are generally considered the most important—and most often measured—nutrient elements. Average concentrations of these elements in seawater are given in Table VII. Nitrogen, phosphorus, and silicon exist in the ocean primarily as the metabolizable compounds nitrate (NO_3^-), phosphate (PO_4^{3-}), and silicate ($Si(OH)_4$). The concentration of these nutrient compounds varies with both depth and location in the ocean, and also changes seasonally in response to increased biological uptake or release. Representative vertical distributions of phosphate, nitrate, and silicates in the Atlantic and Pacific Oceans are shown in Figure 2. These vertical distributions are characterized by four different layers: (1) a surface layer in which

TABLE VI

Solubility of Nitrogen in Seawater in μmol kg^{-1} from Kester, 1975.

t (°C)	Salinity												
	0	4	8	12	16	20	24	28	31	33	35	37	39
−1	844.8	817.2	790.5	764.6	739.6	715.5	692.1	669.4	653.0	642.2	631.6	621.2	611.0
0	822.7	796.0	770.1	745.1	721.0	697.6	674.9	653.0	637.1	626.6	616.4	606.3	596.4
1	801.5	775.7	750.7	726.5	703.1	680.5	658.6	637.3	621.9	611.8	601.9	592.1	582.5
2	781.2	756.3	732.1	708.7	686.0	664.1	642.8	622.3	607.3	597.5	587.9	578.4	569.1
3	761.9	737.7	714.3	691.6	669.7	648.4	627.9	607.9	593.4	583.9	574.6	565.4	556.3
4	743.5	720.1	697.4	675.4	654.2	633.5	613.6	594.3	580.2	571.0	561.9	553.0	544.2
5	725.8	703.1	681.1	659.8	639.2	619.2	599.8	581.0	567.4	558.4	549.6	541.0	532.4
6	708.9	686.9	665.6	644.9	624.9	605.5	586.7	568.5	555.2	546.5	537.9	529.5	521.2
7	692.6	671.3	650.6	630.5	611.1	592.3	574.0	556.3	543.4	535.0	526.7	518.5	510.4
8	677.2	656.5	636.4	616.9	598.0	579.7	562.0	544.8	532.2	524.0	515.9	508.0	500.1
9	662.3	642.2	622.7	603.7	585.4	567.6	550.4	533.6	521.4	513.4	505.6	497.8	490.2
10	648.0	628.4	609.5	591.1	573.2	555.9	539.2	522.9	511.0	503.3	495.6	488.1	480.7
11	634.3	615.3	596.9	579.0	561.6	544.8	528.5	512.7	501.1	493.5	486.1	478.7	471.5
12	621.1	602.6	584.7	567.3	550.4	534.0	518.1	502.7	491.5	484.1	476.8	469.7	462.6
13	608.4	590.5	573.0	556.1	539.6	523.7	508.2	493.2	482.3	475.1	468.0	461.0	454.2
14	596.3	578.8	561.8	545.3	529.3	513.8	498.7	484.1	473.4	466.4	459.5	452.7	446.0
15	584.6	567.5	551.0	534.9	519.3	504.2	489.5	475.3	464.8	458.0	451.3	444.7	438.1
16	573.3	556.7	540.6	525.0	509.8	495.0	480.7	466.8	456.6	450.0	443.4	436.9	430.6
18	552.0	536.2	520.9	506.0	491.6	477.5	463.9	450.7	441.0	434.6	428.4	422.2	416.1
20	532.2	517.2	502.6	488.4	474.7	461.3	448.3	435.7	426.4	420.4	414.4	408.5	402.7
22	513.8	499.5	485.6	472.1	459.0	446.2	433.8	421.7	412.9	407.1	401.4	395.8	390.2
24	496.6	483.0	469.7	456.8	444.2	432.0	420.2	408.6	400.2	394.6	389.2	383.8	378.5
26	480.5	467.5	454.8	442.5	430.5	418.8	407.4	396.4	388.3	383.0	377.7	372.6	367.5
28	465.4	453.0	440.8	429.0	417.5	406.3	395.4	384.8	377.1	372.0	366.9	362.0	357.1
30	451.3	439.4	427.7	416.4	405.4	394.6	384.2	374.0	366.5	361.6	356.8	352.1	347.4
32	438.0	426.6	415.4	404.5	393.9	383.6	373.6	363.8	356.6	351.9	347.3	342.7	338.2

TABLE VII

Average Concentrations of Nutrient
Ions Dissolved in Seawater.

Dissolved Species	Concentration (μmol kg^{-1})
Nitrate–Nitrogen	30
Phosphate–Phosphorus	2
Silicate–Silicon	110
Total Carbon Dioxide	Extremely variable 2350

the concentration is uniformly low as the result of biological uptake, (2) a layer in which the concentration increases rapidly with depth, (3) a layer of maximum concentration that is usually located between 500 and 1500 m, which results from remineralization of organic phosphorus and nitrogen, and (4) a thick bottom layer with relatively little change with depth. These distributions are controlled by a combination of biological removal and release and vertical and horizontal mixing of deep water masses with high nutrient levels.
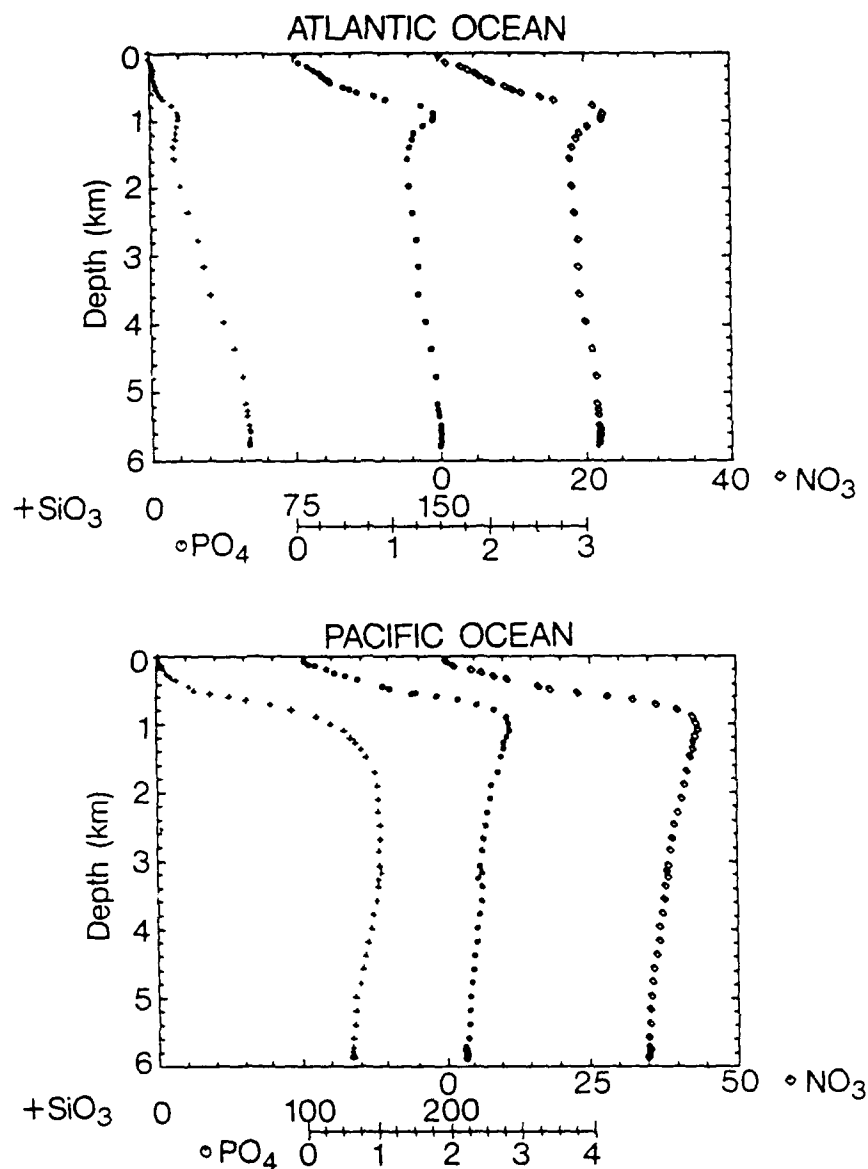
ATLANTIC OCEAN

PACIFIC OCEAN

FIG. 2. Vertical distributions of phosphate (PO_4), nitrate (NO_3). and silicate (SiO_3) in units of $\mu mol\ kg^{-1}$, from GEOSECS stations in the Atlantic Ocean (Sta. 119), from Bainbridge (1981) and Pacific Ocean (Sta. 227), from Craig et al. (1981).

E. Organic Material

Dissolved and colloidal organic compounds have been detected in seawater in concentrations of up to 2 ppm. Concentrations tend to be highest in the near-shore and near-surface waters. Deep water organic material concentrations are nearly constant, with dissolved

organic carbon levels between 200-300 μgC L^{-1} and particulate organic carbon levels less than 10 μgC L^{-1}. Surface values vary seasonally in cycles that are related to the biological cycles. There appear to be two types of dissolved organic material (DOM): young, labile DOM which is released by lysis of cells and older, refractory DOM. In the water column, the combined effects of condensation reactions, metal complexation, microbial degradation and oxidation result in the elimination of the more labile constituents with depth.

About 10% by weight of the DOM in seawater has been identified as common components of living organisms such as free and combined amino acids, carbohydrates, fatty acids, hydrocarbons, steroids, urea and glycolic acid. The bulk of the remainder consists of humic and fulvic acids and other refractory heteropolycondensates, commonly referred to as Gelbstoff, or yellow substances.

At the air-sea interface, dissolved organic material accumulates in a film as a result of adsorption on bubble surfaces and subsequent upward transport. This organic film which forms in the upper few millimeters affects several surface properties of the sea including the surface potential, viscosity and damping of capillary waves. In addition, by reducing evaporation, surface films cause an excess warming of surface waters. Not all of the DOM that sorbs to bubbles reaches the air-water interface. Some of the bubbles collapse or dissolve and the DOM may precipitate to form particulate organic matter (POM).

SALINITY

A. Definition of Salinity

Seawater contains 3.5% salt. Since it is difficult to obtain an exact weight of the salts in seawater by simply evaporating the water (due to inconsistent loss of waters of hydration), salinity is defined operationally. In the past, salinity (S) was defined as "the weight in grams of the dissolved inorganic matter in seawater, after all bromide and iodide

have been replaced by the equivalent amount of chloride and all carbonate converted

to oxide'' (Knudsen, 1901). The usual wet chemical titration method of determining the

chloride ion concentration also measures the concentration of bromide, iodide, and other

trace anions, so a property called chlorinity is used in lieu of the chloride ion concentration.

Chlorinity (Cl) is defined by the amount of silver required to remove all halogen from

0.3285 kilogram (kg) of a seawater sample. Once chlorinity has been determined, salinity

can be calculated (in parts per thousand) using the following relationship:

$$S = 1.80655 \ Cl \ . \tag{5}$$

Chlorinity is also difficult to measure, requiring a chemical titration. Salinity can

be more uniformly defined as a function of electrical conductivity. A "practical salinity"

scale has now been defined as a function of conductivity, or more accurately as a function

of a conductivity ratio.

$$S = 0.0080 - 0.1692 \ K_{15}^{1/2} + 25.3851 \ K_{15} + 14.0941 \ K_{15}^{3/2}$$

$$- 7.0261 \ K_{15}^2 + 2.7081 \ K_{15}^{5/2} \tag{6}$$

constitutes the definition of practical salinity (PSS-78), where $K_{15} = C \ (S, \ 15, \ 0)/C$

$(KCl, \ 15, \ 0)$. $C \ (S, \ 15, \ 0)$ is the conductivity of the sample and $C \ (KCl, \ 15, \ 0)$ is the con-

ductivity of a standard KCl solution at 15°C and atmospheric pressure. Lewis (1980)

gives the algorithms necessary to calculate practical salinity for any given conductivity,

temperature, and pressure.

B. Properties That are a Function of Salinity

Many properties of seawater are affected by changes in salinity. In dilute solution,

colligative properties such as freezing point, osmotic pressure, vapor pressure, and boiling

point depend on the number of particles in solution and not on the nature of the particles.

However, properties such as electrolytic conductance and refractive index depend on the

nature of the dissolved species. The following is a discussion of properties that are a

function of salinity.

(1) Density

Density of seawater changes as a function of both temperature and salinity. An increase in salinity increases the density of seawater. The density of seawater (ϱ) as a function of temperature (°C) and practical salinity (S) can be calculated (kg m^{-3}) from the equation given by Millero and Poisson (1981):

$$\varrho = \varrho_0 + AS + BS^{3/2} + CS^2 \tag{7}$$

where ϱ_0 is the density of pure water (Bigg, 1967) expressed as

$$\varrho_o \ (kg \ m^{-3}) = 999.842594 + 6.793952 \times 10^{-2}t - 9.095290 \times 10^{-3}t^2$$
$$+ 1.001685 \times 10^{-4}t^3 - 1.120083 \times 10^{-6}t^4 + 6.536332 \times 10^{-9}t^5$$

and

$$A = 8.24493 \times 10^{-1} - 4.0899 \times 10^{-3}t + 7.6438 \times 10^{-5}t^2 - 8.2467 \times 10^{-7}t^3$$
$$+ 5.3875 \times 10^{-9}t^4$$

$$B = -5.72466 \times 10^{-3} + 1.0227 \times 10^{-4}t - 1.6546 \times 10^{-6}t^2$$

$$C = 4.8314 \times 10^{-4}.$$

Since the density of dissolved gases is different from that of seawater, addition to and removal of dissolved gases from seawater can also cause changes in density. For example, the addition of nitrogen gas ($\varrho = 0.699$ g cm^{-3} at 25°C) decreases the density of seawater, while the addition of CO_2 ($\varrho = 1.33$) increases it. The density of seawater is about 1.03, so changes in oxygen ($\varrho = 1.03$) concentration have very little effect on seawater density.

(2) Thermal expansion of seawater

The volume of a substance changes with a change in temperature. The relative change of the specific volume is called the coefficient of thermal expansion (α). The thermal expansion of seawater can be calculated from the temperature dependence of its density.

$$\alpha = -\frac{1}{\varrho} \left(\frac{\partial \varrho}{\partial t}\right)_p = \frac{1}{v} \left(\frac{\partial v}{\partial t}\right)_p \tag{8}$$

TABLE VIII

Coefficient of Thermal Expansion of Seawater, $\alpha \times 10^6$ (K^{-1}), as a Function
of Temperature and Salinity at the Sea Surface ($\varrho = 0$), from Millero et al. (1981).

S				$\alpha \times 10^6$ (K^{-1})					
	0°C	5°C	1C°C	15°C	20°C	25°C	30°C	35°C	40°C
0	− 67.95	16.04	88.10	150.91	206.65	257.01	303.14	345.73	384.95
5	− 48.19	31.99	100.83	160.95	214.48	263.02	307.68	349.11	387.41
10	− 30.22	46.82	112.96	170.75	222.25	269.00	312.07	352.03	388.96
15	− 13.12	61.00	124.61	180.21	229.80	274.86	316.41	354.96	390.54
20	3.47	74.67	135.81	189.30	237.08	280.58	320.75	358.07	392.50
25	19.71	87.95	146.59	196.00	244.05	286.12	325.11	361.43	35.02
30	35.75	100.89	156.97	206.30	350.70	291.48	329.50	365.12	398.22
35	51.68	113.54	166.96	214.20	257.01	296.65	333.94	369.17	402.19
40	67.57	125.93	176.58	221.69	262.97	301.63	338.43	373.62	407.00

where ϱ is density, v is volume, t is temperature, and p is pressure. The coefficient of

thermal expansion increases with the increase in salinity at a given temperature. Negative

values of α are found only at low salinities and low temperatures. Seawater under natural

conditions expands with increasing temperature. Table VIII gives the coefficient of thermal

expansion as a function of temperature and salinity.

(3) Freezing point of seawater

The temperature of maximum density $(t_{\varrho max})$ and the freezing point temperature (t_g)

of seawater decrease as salinity increases (Millero and Leung, 1976), as described:

$$t_{\varrho\,max} \, (°C) = 3.95 - 0.200 \, S - 0.0011 \, S^2 \tag{9}$$

$$t_g(°C) = a_o \, S + a_1 \, S^{3/2} + a_2 \, S^2 \tag{10}$$

where $a_o = - 0.0575$, $a_1 = +1.710523 \times 10^{-3}$ and $a_2 = -2.154996 \times 10^{-4}$.

Figure 3 shows the t vs. S relationship for the temperature of maximum density and freezing

point of seawater.

(4) Specific heat

Specific heat (C_p) is defined as the amount of heat (in Joules) required to increase

the temperature of 1 g of a substance 1°C at constant pressure. Specific heat of seawater,

increases with temperature and decreases with salinity and pressure. Table IX illustrates

changes in specific heat as a function of temperature and salinity.
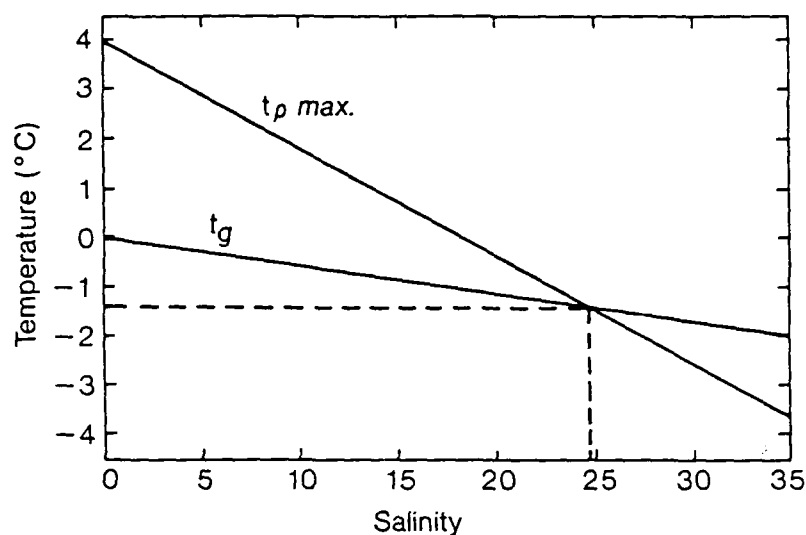
FIG. 3. *Temperature vs. salinity for the temperature of maximum density and freezing point of seawater, from Neumann and Pierson (1966).*

TABLE IX

Specific Heat of Seawater at Constant Pressure (joules gram^{-1} deg^{-1}),
according to Millero et al. (1973).

t (°C)	Salinity						
	0	10	20	25	30	35	40
0	4.2174	4.1466	4.0804	4.0484	4.0172	3.9865	3.9564
5	4.2019	4.1354	4.0730	4.0428	4.0132	3.9842	3.9556
10	4.1919	4.1292	4.0702	4.0417	4.0136	3.9861	3.95CJ
15	4.1855	4.1263	4.0706	4.0437	4.0172	3.9912	3.9655
20	4.1816	4.1247	4.0709	4.0448	4.0190	3.9937	3.9688
25	4.1793	4.1242	4.0717	4.0462	4.0210	3.9962	3.9718
30	4.1782	4.1248	4.0740	4.0494	4.0251	4.0011	3.9775
35	4.1779	4.1252	4.0751	4.0508	4.0268	4.0031	3.9797

(5) Compressibility of seawater

The hydrostatic pressure in the deep ocean is so great that the sea level would rise over 30 meters if seawater were incompressible. In the case where seawater compression occurs slowly, at complete temperature exchange with the surroundings, the coefficient of the isothermal compressibility of seawater, $K = -(\partial V/\partial p)_T/V$, decreases with increase in salinity as shown in Table X. The compressibility of seawater is important in computing sound velocity and adiabatic temperature changes in the ocean.

TABLE X

The Isothermal Compressibility of Seawater ($\beta_T^{\bullet} \times 10^6$) at 1 atm as a Function of
Salinity and Temperature, from Millero et al. (1981).

	$\beta_T^{\bullet} \times 10^6$ (bar^{-1})								
S	0°C	5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°C
0	50.885_0	49.169_2	47.808_6	46.733_1	45.891_8	45.247_2	44.770_7	44.440_4	44.239_1
5	50.179	48.538	47.236	46.203	45.395	44.777	44.320	44.005	43.815
10	49.497	47.928	46.680	45.691	44.915	44.320	43.882	43.580	43.399
15	48.837	47.344	46.138	45.189	44.444	43.873	43.452	43.163	42.990
20	48.190	46.752	45.605	44.696	43.980	43.434	43.030	42.753	42.591
25	47.559	46.182	45.084	44.210	43.525	43.000	42.614	42.352	42.200
30	46.941	45.623	44.570	43.732	43.074	42.572	42.203	41.956	41.818
35	46.335	45.073	44.064	43.260	42.629	42.149	41.799	41.567	41.445
40	45.742	44.534	43.565	42.793	42.188	41.729	41.398	41.185	41.082

(6) Adiabatic temperature change

When seawater is raised from depth to surface, the pressure decreases and the water
sample expands in volume. Since work is performed against the external pressure, the
temperature decreases. This adiabatic cooling or the adiabatic lapse rate Γ (S,t,p)
(°C decibar^{-1}) is defined as the change of temperature per unit pressure for an adiabatic
change of pressure of an element of seawater. From thermodynamic considerations, the
adiabatic lapse rate Γ, a function of pressure, temperature, and salinity can be expressed as

$$\Gamma(S,t,p) = \frac{T\partial V/\partial t}{C_p}$$

where T is absolute temperature (Kelvins), $\partial V/\partial t$ (m^3/(kg °C)) is thermal expansion
and C_p(J/(kg °C)) specific heat of seawater at constant pressure. The lapse rate Γ is
positive except at low salinities and increases with an increase in salinity. Typical values
in the oceanic range are 1-2 $\times$ 10^{-4} °C decibar^{-1}. Adiabatic lapse rates calculated from
the equation of state and specific heat (Bryden, 1973) are given in Table XI. Knowledge
of the adiabatic lapse rate is required to calculate the potential temperature of a water
sample—the temperature of the sample raised to the surface without heat gain or loss.
Algorithms for the calculation of potential temperature (as well as many other proper-
ties of seawater) are given in UNESCO technical paper 44 (Fofonoff and Millard, 1983).

TABLE XI

Adiabatic Lapse Rate, Γ (°C/1000 decibars), when Seawater is Raised 1000 Decibars at 30, 35, and 40 S at different temperatures, calculated from Bryden (1973).

	P decibars	0°C	10°C	20°C	30°C
	0	0.0263	0.1075	0.1790	0.2448
	1000	0.0452	0.1205	0.1874	0.2497
	2000	0.0631	0.1328	0.1954	0.2543
	3000	0.0801	0.1445	0.2031	0.2588
	4000	0.0962	0.1556	0.2104	0.2630
S = 30	5000	0.1113	0.1662	0.2173	0.2671
	6000	0.1256	0.1761	0.2239	0.2710
	7000	0.1389	0.1855	0.2302	0.2747
	8000	0.1512	0.1942	0.2361	0.2782
	9000	0.1627	0.2024	0.2416	0.2815
	10000	0.1732	0.2099	0.2468	0.2846
	0	0.0358	0.1149	0.1843	0.2479
	1000	0.0541	0.1274	0.1923	0.2526
	2000	0.0714	0.1393	0.2001	0.2571
	3000	0.0879	0.1506	0.2074	0.2614
	4000	0.1034	0.1613	0.2144	0.2655
S = 35	5000	0.1180	0.1714	0.2211	0.2695
	6000	0.1316	0.1809	0.2274	0.2732
	7000	0.1443	0.1898	0.2334	0.2767
	8000	0.1562	0.1981	0.2390	0.2801
	9000	0.1670	0.2059	0.2442	0.2832
	10000	0.1770	0.2130	0.2491	0.2862
	0	0.0453	0.1222	0.1895	0.2510
	1000	0.0630	0.1343	0.1973	0.2556
	2000	0.0798	0.1457	0.2047	0.2599
	3000	0.0956	0.1566	0.2118	0.2641
	4000	0.1106	0.1669	0.2185	0.2681
S = 40	5000	0.1246	0.1766	0.2249	0.2718
	6000	0.1377	0.1857	0.2309	0.2754
	7000	0.1498	0.1941	0.2366	0.2788
	8000	0.1611	0.2020	0.2419	0.2820
	9000	0.1714	0.2093	0.2468	0.2849
	10000	0.1808	0.2161	0.2515	0.2877

(7) Thermal conductivity

The coefficient of molecular thermal conductivity, γ, decreases with an increase in salinity. The thermal conductivity, although not normally valid for calculations in the open ocean (due to turbulent motion), is needed for various engineering calculations in desalinization (Millero, 1974). The thermal conductivity of seawater has been measured in the temperature range 0-175°C using a relative hot-wire method (Jamieson and Tudhope, 1970). Smoothed values of thermal conductivity of seawater solutions are given in Table XII. Krummel (1907) reported that at 17.5°C, γ is 1.353×10^{-3} cal cm^{-1} sec^{-1} degree^{-1} at $S = 20$, and it drops down to 1.337×10^{-3} at $S = 40$.

TABLE XII

Values of Thermal Conductivity in mW m^{-1}K^{-1},
from Jamieson and Tudhope, 1970.

t (°C)	0*	0	20	35	40	60	80	100	120	140	160
0	569	571	568	565	565	561	557	553	549	545	541
20	603	603	601	599	599	596	593	590	587	584	581
40	631	630	628	627	627	625	623	621	619	617	614
60	653	650	650	649	649	648	647	646	645	644	642
80	670	665	666	666	666	666	666	666	666	665	665
100	681	676	677	678	678	679	680	681	681	682	682
120	687	682	684	685	686	688	689	691	692	693	694
140	688	683	686	688	689	691	694	696	698	700	702
160	684	680	684	686	687	690	694	697	699	702	705
180	677	673	678	681	682	686	689	693	696	700	703

(column spanning header "Salinity" above columns 0* through 160)

(8) Colligative properties

Colligative properties, which vary depending on the number of particles in solution and not in any way on the nature of these particles, respond in the following way to increases in salinity: freezing point is lowered, osmotic pressure is increased, vapor pressure is lowered, and boiling point is elevated. The colligative properties of seawater are described in detail by Millero and Leung (1976). These properties are useful for estimating molecular weight and evaluating a number of thermodynamic properties of seawater:

Freezing point depression:

$$\Delta t = 0.0575 \ (S) - 1.710523 \times 10^{-3} \ (S)^{3/2} + 2.154996 \times 10^{-4} \ (S)^2 \ . \tag{11}$$

Osmotic pressure (π):

$$\pi = A \ (S) + B \ (S)^{3/2} + C \ (S)^2 \tag{12}$$

where

$$A = 0.70249 + 2.3938 \times 10^{-3}t - 3.7170 \times 10^{-6}t^2$$

$$B = -2.1601 \times 10^{-2} + 4.8460 \times 10^{-6}t - 1.0492 \times 10^{-6}t^2$$

$$C = 2.7984 \times 10^{-3} + 1.5520 \times 10^{-5}t - 2.7048 \times 10^{-8}t^2 \ .$$

Vapor pressure (p):

$$p = p_o + A \ (S) + B \ (S)^{3/2} \tag{13}$$

where

p_o = vapor pressure of pure water (Ambrose and Lawrenson, 1972)

$A = -2.3311 \times 10^{-3} - 1.4799 \times 10^{-4}t - 7.520 \times 10^{-6}t^2 - 5.5185 \times 10^{-8}t^3$

$B = -1.1320 \times 10^{-5} - 8.7086 \times 10^{-6}t + 7.4936 \times 10^{-7}t^2 - 2.6327 \times 10^{-8}t^3$.

Boiling point elevation:

$\Delta t = 0.01645 \ (S)$.   (14)

(9) Surface tension and viscosity

Intermolecular forces that exist in liquids act as cohesive forces within the fluid and as adhesive forces at the boundary surfaces. The cohesive forces determine the viscosity and the adhesive forces, the surface tension of seawater. Surface tension is greater in seawater than in fresh water at a given temperature. The effect of salinity on surface tension is given by Fleming and Revelle (1939):

$Surface\ tension\ (dyne\ cm^{-1}) = 75.64 - 0.144\ t + 0.0399\ (Cl)$.   (15)

The viscosity of seawater increases with increasing salinity and with decreasing temperature. Table XIII gives values of the viscosity coefficient of seawater (η) as a function of temperature and salinity.

(10) Ionic strength

Ionic strength, I, is a measure of the interionic effect resulting primarily from electrical attraction and repulsions between the various ions. Ionic strength of seawater increases directly with salinity according to the following relationship:

$I = \frac{1}{2} \sum_i C_i Z_i^2$ (16)

where C is the ion concentration and Z is the charge. Empirically $I = 0.02\ (S)$.

(11) Gas solubility

The amount of gas dissolved in seawater is a function of both temperature and salinity. Solubility of gases decreases as salinity increases. This can be seen for oxygen and nitrogen by examining Tables V (oxygen) and VI (nitrogen).

TABLE XIII

The Viscosity of Seawater (η) at Various Salinities and Temperatures (in Centipoises) Computed from Values for Distilled Water (η_0) by Korson et al. (1969) Using Equations Developed by Millero (1974), from Riley and Skirrow (1975).

S	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
0	1.7916	1.6739	1.5681	1.4725	1.3857	1.3069	1.2349	1.1691	1.1087	1.0532	1.0020	0.9547	0.9109	0.8703	0.8326	0.7975
5	1.8049	1.6868	1.5808	1.4849	1.3979	1.3189	1.2466	1.1807	1.1200	1.0644	1.0129	0.9655	0.9215	0.8807	0.8428	0.8076
10	1.8180	1.6995	1.5930	1.4968	1.4095	1.3302	1.2576	1.1913	1.1304	1.0745	1.0228	0.9751	0.9309	0.8900	0.8519	0.8165
15	1.8312	1.7122	1.6054	1.5087	1.4210	1.3412	1.2685	1.2018	1.1407	1.0845	1.0327	0.9847	0.9402	0.8991	0.8608	0.8252
20	1.8445	1.7251	1.6178	1.5208	1.4325	1.3525	1.2794	1.2125	1.1513	1.0945	1.0424	0.9942	0.9495	0.9082	0.8697	0.8339
25	1.8579	1.7380	1.6302	1.5327	1.4442	1.3638	1.2903	1.2231	1.1614	1.1046	1.0522	1.0036	0.9588	0.9172	0.8786	0.8426
30	1.8713	1.7509	1.6427	1.5448	1.4560	1.3751	1.3012	1.2338	1.1717	1.1146	1.0619	1.0132	0.9682	0.9263	0.8875	0.8513
32	1.8767	1.7563	1.6478	1.5497	1.4607	1.3797	1.3057	1.2379	1.1758	1.1186	1.0658	1.0171	0.9719	0.9300	0.8910	0.8547
34	1.8823	1.7643	1.6528	1.5545	1.4652	1.3843	1.3101	1.2423	1.1800	1.1227	1.0698	1.0210	0.9757	0.9336	0.8945	0.8582
36	1.8876	1.7696	1.6578	1.5594	1.4701	1.3888	1.3146	1.2465	1.1841	1.1267	1.0737	1.0248	0.9793	0.9372	0.8981	0.8617
38	1.8932	1.7752	1.6630	1.5644	1.4748	1.3934	1.3189	1.2508	1.1883	1.1308	1.0778	1.0286	0.9831	0.9409	0.9017	0.8651
40	1.8986	1.7805	1.6680	1.5692	1.4795	1.3980	1.3233	1.2551	1.1925	1.1348	1.0817	1.0325	0.9869	0.9446	0.9053	0.8686
42	1.9041	1.7861	1.6732	1.5741	1.4842	1.4026	1.3278	1.2595	1.1967	1.1389	1.0857	1.0363	0.9906	0.9483	0.9089	0.8721

Viscosity of pure water η_t at temperature t°C is given by $\log \dfrac{\eta_t}{\eta_{20}} = \dfrac{1.1709\,(20-t) - 0.001827(t-20)^2}{t + 89.93}$ where η_{20} is the viscosity at 20°C.

Viscosity of seawater calculated from ratio $\dfrac{\eta}{\eta_0} = 1 + ACl_v^{1/2} + BCl_v$.

Where Cl_v is the volume chlorinity ($Cl_v = Cl \times$ density) and A = 0.000366, 0.001403 and B = 0.002756, 0.003416 at 5° and 25°C; constants at other temperatures obtained by linear interpolation or extrapolation.

According to Matthaus (1972) the change in dynamic viscosity ($d\eta_t$, centipoises) produced by increase in pressure (P, kg cm⁻² at temperature, T°C) can be calculated from the expression

$d\eta_P = 1.7913 \times 10^{-4}\,P + 9.5182 \times 10^{-8}P^2 + P(1.3550 \times 10^{-5}\,T - 2.5853 \times 10^{-7}T^2 - P^2(6.0833 \times 10^{-9}\,T - 1.1652 \times 10^{-10}T^2)$.

(12) The refractive index

Light rays approaching the water surface from the air are refracted when they pass into the water. The refractive index *(N)* of seawater is an optical property that increases when salinity increases. Measurements of salinity can be made by determining the refractive index of a seawater solution according to an equation developed by Wilson (1975). Miyake (1939) developed an equation:

$$N_{D, 25°} = 1.332497 + 0.000334 \ (Cl) \ , \tag{17}$$

which describes the refractive index of the D line of sodium vapor measured at 25°C, as a function of chlorinity. Some representative values for the absolute refractive index of seawater are given in Table XIV. Leyendekkers (1977) has published a more recent equation that can be used to calculate the absolute refractive index of seawater as a function of wavelength, temperature, pressure, and salinity.

(13) Speed of sound

The speed of sound in seawater has many practical applications because sound is transmitted through great distances in the water. The speed of sound in seawater varies with salinity, temperature, and pressure. The speed of sound increases when salinity increases. This is illustrated in Figure 4. A precise equation for calculating sound velocity in the ocean as a function of salinity, temperature, and pressure is given by Chen and Millero (1977) and is presented in a later section of this paper.

TABLE XIV

Refractive Index of Seawater, for Different
Salinities and Temperatures, at 1 atm, and Wavelength
589.26 nm, as calculated by Leyendekkers (1977).

	Temperature °C		
S	0	15	25
10	1.33637	1.33568	1.33475
20	1.33834	1.33752	1.33655
30	1.34030	1.33936	1.33835
35	1.34127	1.34027	1.33924
40	1.34223	1.34118	1.34014
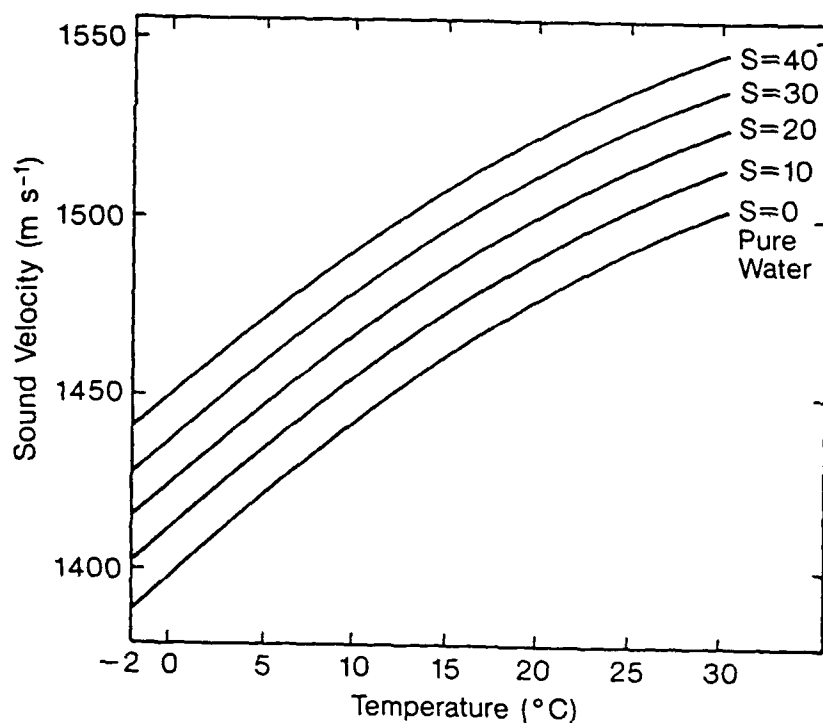
FIG. 4. Velocity of sound (m s⁻¹) in pure water and seawater of different salinity at atmospheric pressure as a function of temperature, from Neumann and Pierson (1966).
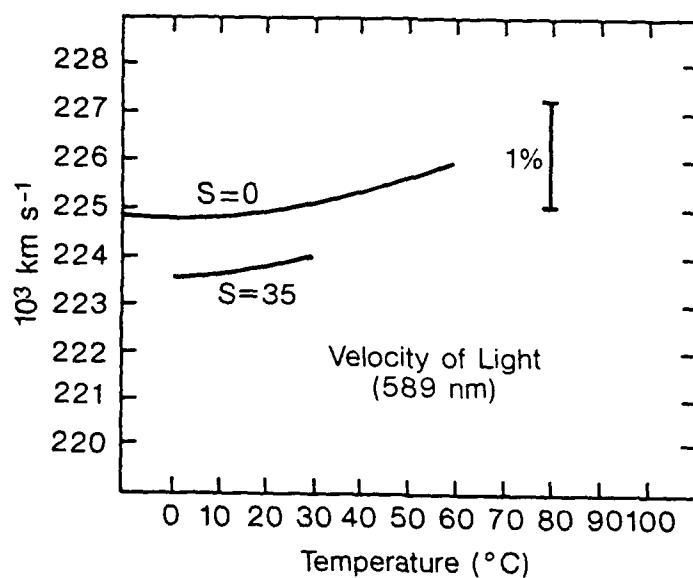
FIG. 5. Velocity of light in pure water and seawater as a function of temperature, from Kalle (1942).

(14) Speed of light

While the velocity of light is constant in a vacuum, it changes in seawater as a function of temperature and salinity. The speed of light decreases as salinity increases, as shown in Figure 5. The refractive index can be used to measure the speed of light in seawater.

(15) Electrical conductivity

As previously discussed, seawater contains an abundance of highly dissociated salts. These salts give seawater a relatively high electrical conductivity that increases almost linearly with salinity. The relationship among temperature, salinity (chlorinity), and conductivity is shown in Figure 6. There is a vast literature on the electrical conductivity of seawater. While the early relationships are relatively good, much of the early data is in error. Recent measurements use potassium chloride (KCl) as an absolute standard and are very precise. Evaluation of the conductivity data used to determine the practical salinity scale has been presented in several papers (Dauphinne, 1980). An algorithm for
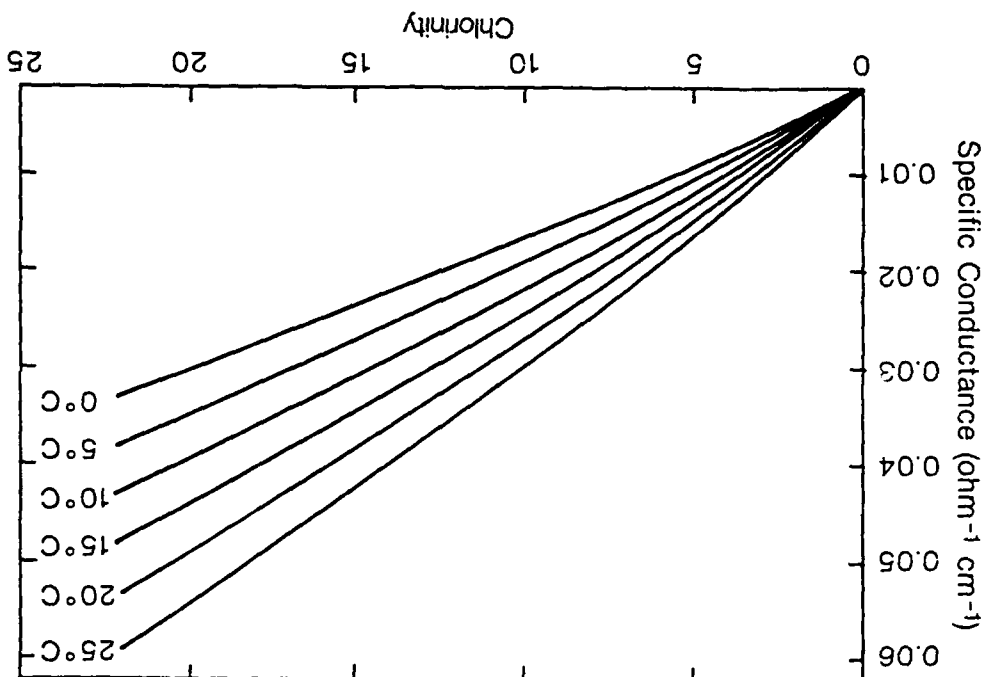
FIG. 6. Specific conductance of seawater at various temperatures and chlorinities, from Thomas et al. (1934).

calculating conductivity from salinity, temperature and pressure is also available (Fofonoff and Millard, 1983).

CHEMICAL PROCESSES IN THE OCEAN

The major components of seawater are generally uniformly distributed in the ocean. However, living organisms and other particles are not. This is significant for chemical processes in the ocean, since most chemical reactions are either biologically controlled or occur at interfaces, or both. Primary productivity, heterotrophic activity (respiration) and microbial degradation (decomposition) are the major biological processes controlling chemical reactions in the ocean. Non-biological chemical reactions in the sea are governed by hydrogen ion activity (pH), oxidation-reduction potential, and solubility.

A. Photosynthesis and Respiration

Oxygen and carbon dioxide are altered reciprocally by photosynthesis and respiration; the overall reaction can be described schematically as:

$$CO_2 + H_2O \underset{respiration}{\overset{photosynthesis}{\rightleftharpoons}} CH_2O + O_2 , \tag{18}$$
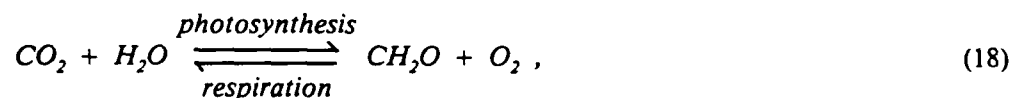
which either produces or consumes organic matter (CH_2O). When light penetrates the upper layers of the ocean, carbon is fixed from carbon dioxide by photosynthesis, a process that requires light and the presence of plant pigments, such as chlorophyll, and yields oxygen and a sugar. Plant material is literally compounded from substances in solution in the water—the carbonate components, and nitrogen and phosphorus compounds. During this process, substantial fractions, or sometimes practically all, of the micronutrients present are organically bound in the bodies of the plants. Once there, they can enter the food web in which the plants are eaten by herbivores, which are in turn eaten by carnivores, and so on. During these particulate stages—when the nutrients are bound as living or dead solid matter—the nutrients can be moved through the water independently of the motion of the water itself by swimming and by gravity. These processes distribute the

nutrients differently from the distribution of the major constituents, which are all distributed essentially identically. The net direction of particle transport is downward to depths below which light penetrates. Below the photic zone, the net biological process is respiration, by which particulate matter is redissolved or returned to the inorganic form (remineralization). These processes constitute a continued downward transport of nutrients. Only the motion of the water itself can return nutrients to the upper, lighted layers where photosynthesis can proceed and the cycle can begin again.

In near-surface layers (generally the upper 25-50 m) oxygen concentrations much higher than those predicted from the solution of air are present, as a result of photosynthesis and air injection from submerged bubbles. In mid-depths (near 1000 m) the oxygen generally decreases to a minimum value. The deep waters of the ocean are generally renewed by waters that were formed by sinking cold waters, which are initially high in oxygen and low in organics.

B. Carbon Dioxide-Carbonate System

Carbon dioxide enters the ocean either from the atmosphere or as a result of animal respiration (Equation 18). As carbon dioxide is added to seawater, it reacts with the water to form carbonic acid.

$$H_2O + CO_2 \rightleftharpoons H_2CO_3 \qquad (19)$$
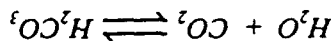
The acid then dissociates in two steps:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad (20)$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad (21)$$
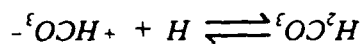
The carbonate (CO_3^{2-}) produced in this process is used by organisms to construct shells of calcium carbonate ($CaCO_3$). Many of these organisms live in surface waters. When they die, their shells fall and carbonate-laden sediments are formed.

One representation of the carbon dioxide-carbonate system is presented in Figure 7. These complex reactions are responsible for controlling the pH of seawater via the hydrogen ion concentration, directly affecting many chemical equilibria in seawater.
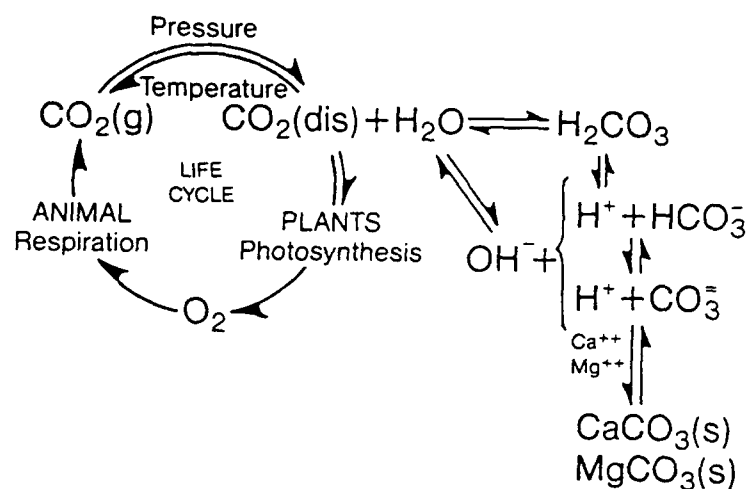
$$\text{CO}_2(\text{g}) \quad \text{CO}_2(\text{dis}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$$

$$\text{OH}^- + \begin{cases} \text{H}^+ + \text{HCO}_3^- \\ \text{H}^+ + \text{CO}_3^= \end{cases}$$

$$\text{CaCO}_3(\text{s})$$
$$\text{MgCO}_3(\text{s})$$

FIG. 7. The carbon dioxide-carbonate system, from Horne (1969).

The changes in the pH of seawater with pressure and temperature can be attributed to shifts of equilibria in the carbonate system together with changes in the dissociation of $CaCO_3$ and $MgCO_3$.

The pH of seawater is slightly basic due to the presence of excess cations of strong bases. Seawater has a pH of 8.0 to 8.2 at the surface and decreases to 7.7 to 7.8 at depths of several thousand meters. The carbonate system (Figure 7) plays a large role in controlling the pH of seawater. Since carbonate reactions are equilibrium reactions, the carbonate system acts like a buffer to resist large changes in the pH of seawater.

C. Adsorption

Changes on the surfaces of well-defined solids exposed to seawater from diverse sources have been observed by microelectrophoresis, ellipsometry and contact angle measurements. These observations indicate that an adsorbed organic film forms rapidly on all exposed surfaces, which lowers surface energy and imparts a moderately negative electrical charge. This molecular fouling is instantaneous. Based on "thickness" measurements, molecular fouling can have no significant effect on fluid flow or heat transfer. Nevertheless, the surface properties resulting from adsorption of an organic

film may affect the sequence of microbial events that follow and that are known to impact both of these engineering parameters (Characklis, 1981). Thin, viscoelastic biofilms develop on conduit walls and cause unexpectedly large increases in fluid frictional resistance. Concomitant with the adsorption of organic moieties is the coadsorption of ions to prevent charge accumulation.

Dissolved organic and inorganic substances in seawater also sorb on the surface of bubbles in sufficient quantities to form colloidal micelles or aggregates of molecules. The sorption of organic material on bubbles and particulate forms results in removal of phosphates from seawater and forms an important link in the food chain in the sea. The bursting of bubbles is believed to be the chief mechanism for the formation of particulate matter in the marine atmosphere. The relative proportions of the major elements in the marine aerosol have been found to deviate rather substantially from the virtually constant relative proportions of the major ions in seawater. In the marine atmosphere, concentration levels of total particulate matter have been measured up to and exceeding $100 \ \mu g \ m^{-3}$, depending on such variables as wind speed, relative humidity and sea state. Major element concentrations of marine aerosols are generally of the order of $1 \ \mu g \ m^{-3}$ with chlorine, the principle element, present in the range of $1\text{-}10 \ \mu g \ m^{-3}$ near sea level for wind velocities up to $10 \ m \ s^{-1}$. The identity and movement of organic compounds in the particulate or gas phase of the marine atmosphere are known in considerably less detail than those of elemental composition.

D. Oxidation-Reduction

Oxidation-reduction refers to the loss and gain of electrons, respectively, from the outer orbital shells of the reacting atoms. Because both the partial pressure of O_2 in the atmosphere and the oceanic pH are fixed, the oxidation-reduction potential of seawater (E_h) is relatively constant. Cooper and Zika (1983) suggested that photochemically produced hydrogen peroxide and superoxide radical are also important in the maintenance

TABLE XV

Average Rates of Deterioration of Sheet Pile Structures, from U.S. Navy Design Manual (1971).

Factors affecting deterioration		Types of structure		
		Harbor bulkheads (in. per yr.)	Beach bulkheads (in. per yr.)	Groins and jetties (in. per yr.)
Geographical location	Southern region	0.0062	0.017	0.018
	Northern region	0.0023	0.0075	0.011
Zone relative to tidal planes	8 ft above M.H.W.	0.0049	0.020	0.010
	5 ft to 8 ft above M.H.W.	0.0049	0.022	0.010
	2 ft to 5 ft above M.H.W.	0.0049	0.0081	0.010
	M.H.W.	0.0027	0.0074	0.0055
	Mean tide level	0.0024	0.001	0.024
	M.L.W.	0.0035	0.002	0.028
	M.L.W. to ground line	0.0035	0.0035	0.0035
	Below ground line	0.002	0.002	0.002
Sand, earth, or other cover	No cover on either surface of pile	0.0075	0.027	0.019
	One surface never covered, other covered part time	0.0076	0.020	0.014
	One surface only covered	0.0026	0.0094	0.020
	One surface always covered, other covered part time	–	0.0065	0.0057
	Both surfaces covered part time	–	–	0.017
	Both surfaces always covered	–	0.0017	0.0026
Exposure to salt spray	Heavy spray	0.0083	0.016	0.016
	Moderate spray	0.0041	–	
	Light spray	0.0024	–	
Painting	None	0.0045	0.018	0.020
	At least once	0.0027	0.011	0.010

of E_h of natural waters high in organic matter. At a pH of 8 and an O_2 partial pressure of about 0.2 atm, the E_h of seawater is about 0.75 volt and is governed by the following reaction:

$$2H_2O = O_2 + 4H^+ + 4 \; electrons \; . \tag{22}$$

All oxidation-reduction reactions in the open sea, including corrosion, are controlled by this half-cell reaction. Corrosion is generally due to an electrochemical process whereby atoms of a given metal lose electrons (oxidation), which then combine with atoms of another element (reduction). The migration of electrons from an anodic area to a cathodic area may be caused or accelerated by the chemical, physical, and biological properties of seawater. Increases in temperature, salinity, and dissolved oxygen content accelerate corrosion. Table XV lists some typical corrosion rates for types of steel structures as affected by geographic location, tidal range, earth cover, exposure, and protective coatings. However, corrosion rates rarely fall within predetermined ranges; instead, corrosion tends

to be a highly localized phenomenon. The roles of oxygen, biological activity, temperature, velocity, salinity, and pH in the uniform and localized corrosion of specific metals are discussed by Schumacher (1979).

ACOUSTIC RELAXATION PROCESSES IN SEAWATER

In traveling through seawater an acoustic signal is subject to two types of degradation: (1) change in the direction of the sound wave as a result of dispersion, scattering, and reflection; and (2) absorption, which represents a reduction of the energy level of the sound. Velocity of sound in a liquid depends on both density and compressibility. Temperature, pressure, and salinity, parameters that impact density and compressibility, determine the velocity of sound in seawater. Their relative importance is shown in the first-order terms in the empirical seawater sound velocity (U) equation given by Chen and Millero (1977):

$$U(S,t,p) = C_w(t,p) + A(t,p)S + B(t,p) S^{3/2} + D(t,p)S^2 \tag{23}$$

$$C_w(t,p) = C_{00} + C_{01}t + C_{02}t^2 + C_{03}t^3 + C_{04}t^4 + C_{05}t^5 \tag{24}$$
$$+ (C_{10} + C_{11}t + C_{12}t^2 + C_{13}t^3 + C_{14}t^4) \, p$$
$$+ (C_{20} + c_{21}t + C_{22}t^2 + C_{23}t^3 + C_{24}t^4) \, p^2$$
$$+ (C_{30} + c_{31}t + C_{32}t^2) \, p^3$$

where:

$C_{00} = + 1402.388$

$C_{01} = + 5.03711$

$C_{02} = - 5.80852 \times 10^{-2}$

$C_{03} = + 3.3420 \times 10^{-4}$

$C_{04} = - 1.47800 \times 10^{-6}$

$C_{05} = + 3.1464 \times 10^{-9}$

$C_{10} = + 0.153563$

$C_{11} = + 6.8982 \times 10^{-4}$

$C_{12} = - 8.1788 \times 10^{-6}$

$C_{13} = + 1.3621 \times 10^{-7}$

$C_{14} = - 6.1185 \times 10^{-10}$

$C_{20} = + 3.1260 \times 10^{-5}$ $C_{30} = - 9.7729 \times 10^{-9}$

$C_{21} = - 1.7107 \times 10^{-6}$ $C_{31} = + 3.8504 \times 10^{-10}$

$C_{22} = + 2.5974 \times 10^{-8}$ $C_{32} = - 2.3643 \times 10^{-12}$

$C_{23} = - 2.5335 \times 10^{-10}$

$C_{24} = + 1.0405 \times 10^{-12}$

$$A(t,p) = A_{00} + A_{01}t + A_{02}t^2 + A_{03}t^3 + A_{04}t^4 \tag{25}$$
$$+ (A_{10} + A_{11}t + A_{12}t^2 + A_{13}t^3 + A_{14}t^4)\, p$$
$$+ (A_{20} + A_{21}t + A_{22}t^2 + A_{23}t^3)\, p^2$$
$$+ (A_{30} + A_{31}t + A_{32}t^2)\, p^3$$

where:

$A_{00} = + 1.389$ $A_{10} = + 9.4742 \times 10^{-5}$

$A_{01} = - 1.262 \times 10^{-2}$ $A_{11} = - 1.2580 \times 10^{-5}$

$A_{02} = + 7.164 \times 10^{-5}$ $A_{12} = - 6.4885 \times 10^{-8}$

$A_{03} = + 2.006 \times 10^{-6}$ $A_{13} = + 1.0507 \times 10^{-8}$

$A_{04} = - 3.21 \times 10^{-8}$ $A_{14} = - 2.0122 \times 10^{-10}$

$A_{20} = - 3.9064 \times 10^{-7}$ $A_{30} = + 1.100 \times 10^{-10}$

$A_{21} = + 9.1041 \times 10^{-9}$ $A_{31} = + 6.649 \times 10^{-12}$

$A_{22} = - 1.6002 \times 10^{-10}$ $A_{32} = - 3.389 \times 10^{-13}$

$A_{23} = + 7.988 \times 10^{-12}$

$$B(t,p) = B_{00} + B_{01}t + (B_{10} + B_{11}t)\, p \tag{26}$$

$B_{00} = - 1.922 \times 10^{-2}$ $B_{10} = + 7.3637 \times 10^{-5}$

$B_{01} = - 4.42 \times 10^{-5}$ $B_{11} = + 1.7945 \times 10^{-7}$

$$D(t,p) = D_{00} + D_{10}\, p \tag{27}$$

$D_{00} = + 1.727 \times 10^{-3}$ $D_{10} = - 7.9836 \times 10^{-6}$

for the ranges temperature *(T)* = 0 to +40°C, pressure *(p)* = 0 to 10,000 decibars, and salinity *(S)* = 0 to 40.

In addition, large concentrations of bubbles can alter density and compressibility and, thus, the sound-propagating properties of fluids. However, dissolved gases have a negligible effect on the velocity of sound in seawater.

In the presence of density or compressibility gradients in the sea, sound waves are refracted toward the region of lower velocity. Because pressure increases with depth and because temperature and salinity profiles are complex, the profiles of sound propagation tend to be complex. Figure 8 is a composite of sound propagation profiles that might be encountered in (a) an isothermal, (b) a surface duct, (c) bottom bounce, and (d) a deep sound channel.

Sound attenuation (α) in a fluid can be predicted by hydrodynamic theory:

$$\alpha/f^2 = 8\pi^2 \ \frac{\mu V_S}{3V^3} \tag{28}$$

where f, μ, V_S, and V are frequency, shear viscosity, specific volume, and velocity of sound, respectively. Sound absorption in liquids is typically given as $\alpha \ f^{-2}$ in units of nepers second squared per centimeter ($sec^2 \ cm^{-1}$) where α is the attenuation coefficient in nepers cm^{-1} and f^2 is the frequency in hertz (Hz). Previous measurements in pure (distilled) water have shown that ultrasonic absorption is typically 20×10^{-17} nepers $sec^2 \ cm^{-1}$, three times as large as would be predicted by the value calculated from the equation (Herzfeld and Litovitz, 1959).

A small amount of the absorption is due to viscous losses; however, the majority of the increased absorption is attributed to "structural" relaxation. Water is envisioned to be made of monomers, dimers, etc., of H_2O molecules. When an ultrasonic wave passes through the liquid, the equilibrium distribution of these groupings is perturbed. All relaxation processes are characterized by a relaxation time, τ, the time required for

(A) Isothermal ("Normal Mode") Propagation

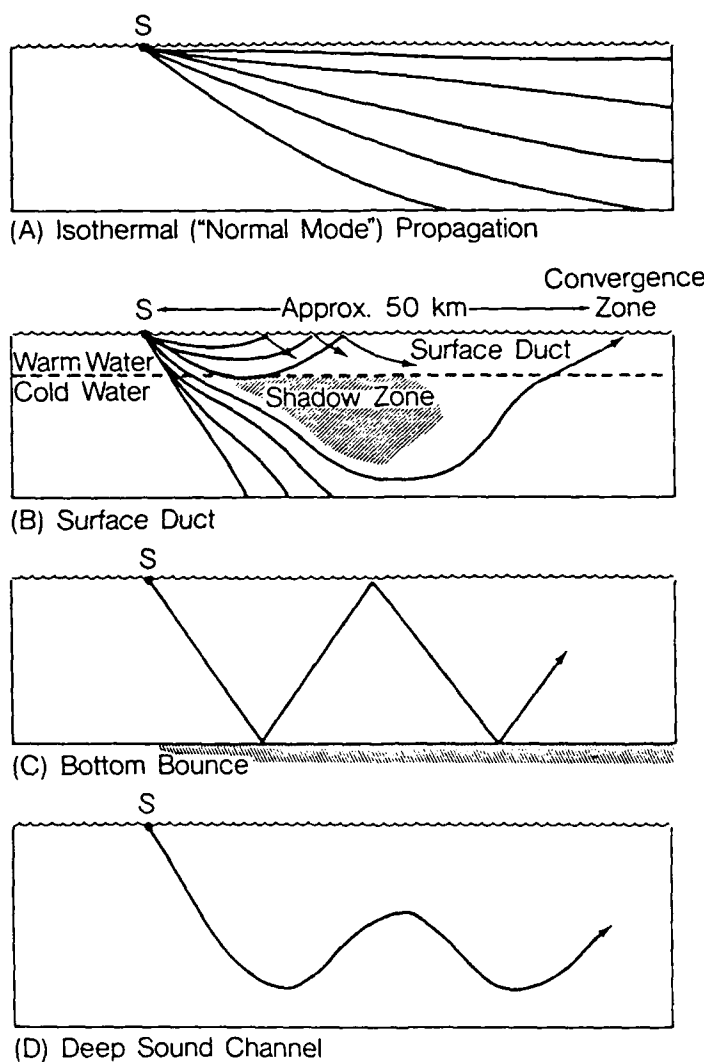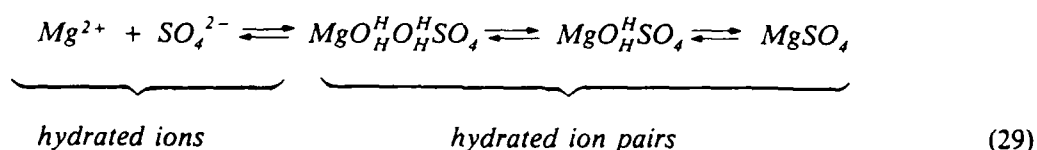(B) Surface Duct

(C) Bottom Bounce

(D) Deep Sound Channel

FIG. 8. Some sonar paths in the sea, from Horne (1969).

the distribution to return to e^{-1} of its initial value, or a relaxation frequency, f^x, which is equal to $\frac{1}{2}\pi\,\tau$. Return to equilibrium takes time so that the energy required to disturb the system is returned to the ultrasonic wave slightly out of phase. This relaxation leads to absorption. In seawater, measured absorption at 10 kHz (Mellen *et al.*, 1979) is typically 2 dB km^{-1} or 2000 x 10^{-17} nepers sec^2 cm^{-1}. At 50 kHz, the attenuation is near 400 x 10^{-17} nepers sec^2 cm^{-1} and decreases further at higher frequencies.

Thermal relaxation is associated with transfer of energy to (or from) internal degrees of freedom of the molecule (vibrations or rotations). An ultrasonic wave disturbs the population of these energy states, which return to equilibrium with a characteristic relaxation time, τ. The rate at which energy can be exchanged between translation and these internal modes is limited by τ so the specific heat of the fluid (which depends upon the number of active degrees of freedom) becomes frequency dependent. The attenuation due to this mechanism is proportional (below the relaxation frequency) to the relaxation time and relaxing specific heat. This effect is especially large for hindered internal molecular rotations with long relaxation times.

Enhanced attenuation in seawater relative to pure water can be attributed to another type of relaxation process, chemical relaxation, which results from chemical reactions among the salts in the ocean. Salts, such as $MgSO_4$, have exhibited strong attenuation properties in seawater by profoundly altering the structure of water in their immediate vicinity. These bulky, hydrated aggregates appear to be too large to fit into the available distribution of hole sizes in liquid water. These aggregates exhibit numerous vibrational modes with bond making and breaking.

$$Mg^{2+} + SO_4^{2-} \rightleftharpoons MgO_H^H O_H^H SO_4 \rightleftharpoons MgO_H^H SO_4 \rightleftharpoons MgSO_4$$

$$\underbrace{\hphantom{Mg^{2+} + SO_4^{2-}}}_{\textit{hydrated ions}} \qquad \underbrace{\hphantom{MgO_H^H O_H^H SO_4 \rightleftharpoons MgO_H^H SO_4 \rightleftharpoons MgSO_4}}_{\textit{hydrated ion pairs}} \qquad (29)$$

These reactions are quite slow, so the relaxation time, τ, is large. The relaxation frequencies for the ion pairs lie near 20-150 kHz. Up to this frequency, the absorption increases linearly with f. Above this frequency, the contribution due to chemical relaxation becomes nearly constant at 5-10 dB km^{-1}. Ultrasonic absorption depends on the relative distribution of the $MgSO_4$ ion-pairs (Eigen and Tamm, 1962). Fisher (1972) has shown that a decrease in ultrasonic absorption can be expected as a result of increased hydrostatic pressure with depth, even though the concentration of ion-pairs increases.
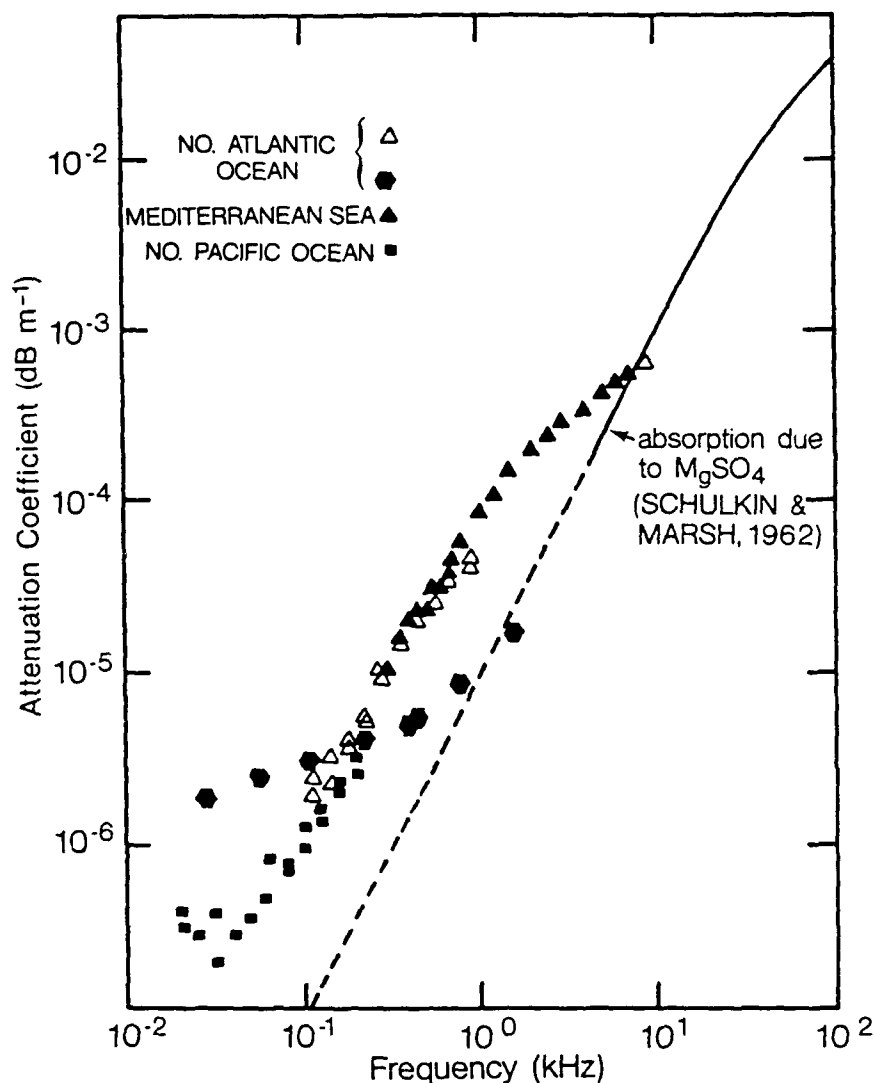
FIG. 9. Sound absorption plot developed by Thorp (1965). The Schulkin and Marsh (1962) calculated curve is based on a depth of 1220 m, T = 4°C and S = 35.

Thorp (1965) compiled data from several authors who had made a series of open ocean sound absorption measurements in the Atlantic, Pacific, and Mediterranean areas at frequencies below the absorption peak for $MgSO_4$ (Figure 9). The at-sea data indicate increased absorption over the expected $MgSO_4$ effect at low frequency, with variability among water masses. The mechanism for the observation is unresolved.

TABLE XVI

Production of Chemicals from Seawater, from McIlhenny (1975).

Commodity	Total annual world production	Annual production from seawater	% of total	Annual value of seawater production
	(metric tons)	(metric tons)		($)
Salt (NaCl)	138874000	39100000[a]	29	280000000
Magnesium (Mg)	201000	121000[b]	60	77000000
Water (H$_2$O)	338000000	284000000	84	75000000
Magnesium compounds (MgO)	10900000[a]	660000[a][b]	6	48000000
Bromine (Br)	132000	36000	27	20700000
Total		324000000		500700000

[a] Estimated
[b] Includes magnesium from dolomitic lime

EXTRACTION OF ELEMENTS AND COMPOUNDS FROM SEAWATER

Processes have been proposed or developed for extracting all the major components

and many of the minor and trace elements from seawater. A survey made by Christensen

and co-workers (1967) of brine processing technology revealed that the following relatively

small number of basic methods are actually being used for the separation of inorganic

materials from seawater: adsorption, evaporation, distillation, solvent extraction, ion

exchange, precipitation, electrolysis, flotation, oxidation, and electroanalytical procedures.

The feasibility of a particular recovery technique depends primarily on the economic attrac-

tiveness of seawater as a raw material, rather than on the existence of suitable recovery

and processing technology. Seawater is a suitable raw material for many major compounds,

but because of capital and energy requirements, it has been estimated that the recovery

of any element lower in concentration than strontium cannot be profitable.

Sodium chloride, sodium carbonate, and bromine, as well as the salts of potassium

and magnesium were first recovered in industrial quantities from seawater. Marine algae

were, for a period, the major industrial source for iodine, bromine and potash. The present

scale of producing chemicals from seawater is considerable. Table XVI summarizes the

major constituents currently recovered on a commercial basis. In addition, gypsum and

potassium compounds are recovered in lesser amounts, and heavy water (D_2O) has been produced on an industrial scale.

Several methods for isolating and concentrating adsorbable organics from aquatic sources have been attempted. Macroreticular resins such as XAD have been used extensively. Ion-exchange celluloses, nylon cloths, germanium prisms, and metal foils have been used to concentrate these materials, which were then characterized by internal reflection infrared spectroscopy, ^{13}C solid phase nuclear magnetic resonance (NMR), pyrolysis-mass spectrometry and thin layer chromatography.

ACKNOWLEDGMENTS

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Engineering materials exposed to seawater are subjected to various deteriorating reactions throughout their lifetime. Chemical reactions that take place in seawater can be attributed to the solvent properties of water, ion-water and ion-ion interactions. Many properties of seawater, such as density, thermal expansion, temperature of maximum density, viscosity, speed of sound, vapor pressure, etc., change with changing salt content. A knowledge of the way these parameters change, as well as processes that cause the changes, is essential to the design of systems that will effectively operate in the ocean. The following is a synopsis of the chemical and physical properties of seawater that are known to have an impact on ocean engineering.

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